

11/10/05

10/510264

DT05 Rec'd PCT/PTO 05 OCT 2004

METHOD FOR CONTINUOUS PREPARATION OF NANOMETER-SIZED  
HYDROUS ZIRCONIA SOL

Technical Field

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The present invention relates to a method for preparation of a nanometer-sized hydrous zirconia sol, particularly a method for continuous preparation of a nanometer-sized spherical hydrous zirconia ( $ZrO_2 \cdot nH_2O$ :  
10 hydrated zirconia or zirconia hydrate) sol required for preparing fine particles of a pure zirconia ( $ZrO_2$ ) or a zirconia-based composite metal oxides, which are used as basic material for functional ceramics such as abrasives, abrasion-resistant materials, solid-state  
15 electrolytes in fuel cell, sensor, coatings and the like; and structural ceramics such as mechanical parts, optical connectors, artificial teeth and the like.

The present invention relates, more particularly, to a method for continuous preparation of spherical  
20 hydrous zirconia in the form of sol having an average particle size (diameter) of about 1~1,000 nm and a small particle size distribution.

A hydrous zirconia sol is a solution wherein hydrous zirconia particles having a diameter of about  
25 1~1,000 nm are dispersed in a colloidal state. And the

hydrous zirconia may be prepared by precipitation of a zirconium salt used as precursor (starting material) in an aqueous solution.

5 The hydrous zirconia sol may be pH-controlled, washed, separated or concentrated to be applied as various materials such as (i) electronic materials or coating materials in the form of stabilized sol itself, (ii) functional ceramics or electronic materials in the form of monodispersed, nanometer-sized powder subjected  
10 to drying and/or calcination, (iii) materials for catalysts or batteries/cells subjected to surface-modification by coating, (iv) functional ceramics or structural ceramics in the form of composite materials combined with other components, and the like.

15 To provide a method for effectively preparing the said multi-purpose hydrous zirconia sol is important for processing effectiveness, preparation cost and quality of the final product.

20 Recently, there are required monodispersed spherical particles of the hydrous zirconia having a sphere-like shape, a nanometer-sized average particle diameter and a small particle size distribution in consideration of the usage and quality of zirconia ceramics.

## Background Art

There have been various conventional methods for preparing hydrous zirconia sol, for example, pH-controlled co-precipitation, forced hydrolysis, alkoxide-based sol-gel process and hydrothermal method.

The pH-controlled co-precipitation is provided for preparing the particles of zirconia-based composite metal oxides. However, this method has many problems in that the co-precipitates having a uniform composition in each particle can be hardly obtained, that the co-precipitates prepared after neutralization can be hardly filtered and separated since they are susceptible to gellation, and that the anion impurities can be hardly removed with water.

Moreover, the pH-controlled co-precipitation has problems that the separated particles can hardly be crushed in a desired size since they are agglomerated into a hard lump during calcination, and thus increasing the possibility for the contamination of impurities therein during pulverization of the lump, thereby deteriorating the quality of the particles.

In the widely applied forced hydrolysis, a reaction time should be long enough to increase a reaction yield. Moreover, since the metallic compounds

to be introduced as a stabilizer cannot be completely precipitated and its components are eluted out in the course of separation and washing of the precipitates, the composition required in the zirconia particles product cannot be suitably controlled.

Further, in the conventional hydrolysis method, the hydrous zirconia particles prepared in the course of the reaction agglomerate easily with each other, and the degree of agglomeration becomes more severe during separation and drying after the reaction. There is known an azeotropic dehydration method employing organic solvents having a boiling point equal to that of water to prevent the said agglomeration among the particles. But, this method cannot completely solve the problem.

According to the recent report as disclosed in "Y. T. Moon et al, *J. Am. Ceram. Soc.*, 78(4), 1103-1106 and 78(10), 2690-2694 (1995)", a precipitation method may be effectively employed for the preparation of hydrous zirconia sol. In the precipitation method, organic solvents such as alcohols to be used in addition to water can lower the precipitation temperature while lowering the solubility of the zirconium salts used as starting materials, since they have low dielectric constant.

The said article is based on a precipitation

method using a water-alcohol mixture as solvent, and discloses that narrowly distributed spherical hydrous zirconia sol having an average diameter of 0.28  $\mu\text{m}$  can be obtained in a batchwise manner by rapidly heating within a microwave oven the reaction mixture in a beaker without stirring.

The present inventors repeated the same procedure as the said article. Their experimental results revealed that the agglomeration severely occurred among the hydrous zirconia particles that are generated belatedly after an initial precipitation occurs according to the rapid rise of temperature, although the same zirconium salt solution was heated rapidly within a microwave oven in a disturbance-free, static state without flow or stirring, and that the particle size distribution was large thereby.

The present inventors discovered that the quality of the hydrous zirconia particles obtained was more deteriorated at a larger volume of the solution tested, and that local temperatures within the disturbance-free aqueous solution were not uniformly raised despite of the microwave heating. Although a uniform heating by microwave may be achievable when the volume of the aqueous solution is very small, the effectiveness of uniform heating by microwave was gradually reduced as

its volume was increased.

Yet, there has not been known a method for continuous preparation of a sol of spherical hydrous zirconia particles with an average diameter less than about 250 nm and a small particle size distribution based on the precipitation method using a water-alcohol mixture as solvent.

Alternatively, zirconium alkoxides such as zirconium butoxide ( $\text{Zr}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$ ) may be used as a starting material instead of a zirconium salt. However, this alkoxide-based sol-gel process is not adequate for a commercial bulk preparation because of its too expensive cost.

A hydrous zirconia sol can also be prepared in a hydrothermal method. USP 5,275,759 (1994) to S. Osaka et al. discloses that a hydrous zirconia sol can be prepared from an aqueous solution containing zirconium salts and urea in the hydrothermal method at a temperature of 60~300 °C and under pressure. However, the hydrothermal method for preparing a hydrous zirconia sol has a problem in economical feasibility, since it requires an expensive hydrothermal apparatus and very long reaction time. Further, serious particle agglomeration is observed after calcination of the particles of the hydrous zirconia sol obtained by the

hydrothermal method, since the size of hydrous zirconia particles is too small and their size distribution is broad.

5        These conventional methods for preparing a hydrous  
zirconia sol cannot provide a means for bulk preparation  
of hydrous zirconia sol required for preparation of  
spherical zirconia particles having an average diameter  
less than about 250 nm and a small particle size  
distribution. Meanwhile, the shape of hydrous zirconia  
10       particles in a state of sol has a close relation with  
size, shape and size distribution of finally obtained  
pure zirconia particles or zirconia particles compounded  
with other metal oxides; and with the degree of  
agglomeration among the particles. Therefore, it is  
15       required to develop a method for continuous preparation  
of hydrous zirconia sol to commercially prepare pure  
zirconia particles or zirconia particles compounded with  
other metal oxides. In this method, a sol of hydrous  
zirconia particles with a nanometer-sized average  
20       diameter, a narrow size distribution and a low degree of  
agglomeration among the particles should be prepared.

#### Disclosure of the Invention

25       An object of the present invention is to provide a

method for preparation of a nanometer-sized spherical hydrous zirconia sol having an average diameter of about 1 to 1,000 nm and a small particle size distribution.

Another object of the present invention is to provide a method for continuous preparation of an excellent hydrous zirconia sol which can be applied as various materials such as (i) electronic materials or coating materials in the form of stabilized sol itself, (ii) functional ceramics or electronic materials in the form of monodispersed, nanometer-sized powder subjected to drying and/or calcination, (iii) materials for catalysts or batteries/cells subjected to surface-modification by coating, (iv) functional ceramics or structural ceramics in the form of composite materials combined with other components, and the like.

As a result of the present inventors' extensive studies, they have now found that a spherical hydrous zirconia sol having a nanometer-sized average diameter and a small particle size distribution can be obtained by uniformly heating the aqueous solution of a zirconium salt, which is maintained in a state of a certain flow, to a temperature higher than its precipitation temperature. The present invention is attained on the basis of these findings.

A particle size distribution of the particles to



be precipitated in the flowing aqueous solution of a zirconium salt is controlled to be small and the agglomeration of the particles obtained thereby is unnoticeable, despite the flow rate is non-uniform due to the shear stress imposed by the solid inner wall of the reactor upon the flow. These are also new findings.

The present invention provides a method for continuous preparation of a well dispersed spherical hydrous zirconia particles with an average diameter( $d_p$ ) of 1~1,000 nm in the form of sol, which method comprises supplying the aqueous solution of a zirconium salt at a concentration of 0.001~0.5 mole/l to a reactor consisting of one or more than two reaction tubes at a temperature less than about 25 °C, heating the said aqueous solution in the reactor(s) up to the boiling point or less, and then discharging the said solution through the outlet of the said reactor(s).

The said aqueous solution of a zirconium salt in the reactor(s) may be heated to about 70~100 °C.

An average diameter( $d_p$ ) of the hydrous zirconia particles prepared according to the present invention may be in the range of 10~250 nm.

The cross-section of a reaction tube used in the present invention may have a circular or concentric annular form. The said aqueous solution of a zirconium

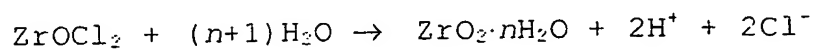
salt flows in the said reactor(s). If the diameter of the circle or the equivalent diameter of the annular area is represented as D, the value D is preferred to be selected within about 0.01~3 cm.

5        According to the present invention, a dispersant may be added to the said aqueous solution of a zirconium salt at the concentration of 0.05~20 g/l.

10        According to the present invention, a starting material, that is, a zirconium salt to be used as zirconia precursor is not limited, as long as it is water soluble. The zirconium salts include, for example, zirconium oxychloride or zirconyl chloride ( $\text{ZrOCl}_2$ ), zirconium tetrachloride ( $\text{ZrCl}_4$ ), zirconyl nitrate ( $\text{ZrO}(\text{NO}_3)_2$ ), zirconium sulfate ( $\text{Zr}(\text{SO}_4)_2$ ) and the like.  
15        Zirconium oxychloride is most widely used.

When zirconium oxychloride is used as the zirconium salt, hydrolysis to proceed in an aqueous solution can be represented as the following reaction formula:

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As illustrated in the above formula, 1 mole of  $\text{ZrOCl}_2$  is changed to hydrous zirconia ( $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ ) with 2  
25        moles of " $\text{H}^+$ " and " $\text{Cl}^-$ " ions being prepared respectively.

Water is generally used as a solvent for the precipitation, since the zirconium salt is very soluble in water at low temperature. When only water is used as the solvent, the precipitation temperature and dielectric constant are high. Then, alcohol can be preferably used with water to lower the precipitation temperature and dielectric constant. Alcohols to be used with water include, for example, ethyl alcohol, propyl alcohol (1-propyl alcohol or 2-propyl alcohol), butyl alcohol and the like.

The composition ratio of water-alcohol mixture used for the aqueous solution of a zirconium salt may be decided in consideration of the average diameter of desired hydrous zirconia particles, concentration of zirconium salt, washing and concentration of sol to be prepared, separation and purification of solvent, regeneration cost and the like.

The mole ratio of the alcohol/water solvent to be used in the present invention is preferably in the range of about 0.5~2.0. Confining the particles having an average diameter less than 100 nm according to the general definition of "nanoparticles", the mole ratio of alcohol/water not less than about 0.7 is preferred for preparation of a sol of hydrous zirconia nanoparticles without significantly lowering the concentration of the

zirconium salt.

5       The stabilizers such as halide (chloride and bromide, etc.), carbonate and nitrate of Y, Ce, Ca or Mg may be further added to the aqueous solution of a zirconium salt depending on usage of the hydrous zirconia to be prepared. Generally, the stabilizers are added so that the amount of the finally prepared oxides such as  $Y_2O_3$ ,  $CeO_2$ ,  $CaO$  and  $MgO$  may be up to 30 mole % on the basis of  $ZrO_2$ .

10       According to the present invention, continuous preparation of a hydrous zirconia sol from the aqueous solution of a zirconium salt can be carried out in a tubular reactor consisting of one or more than two reaction tubes.

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#### Brief Description of the Drawings

20       The above objects, other features and advantages of the present invention will become more apparent by describing the preferred embodiment thereof with reference to the accompanying drawings, in which:

25       Fig.1 is a schematic drawing illustrating a basic construction of a tubular reactor to be used in the present invention;

Fig.2 is a graph showing a temperature change in the aqueous solution of a zirconium salt on the length direction(z) of the reaction tube according to the present invention;

5        Fig.3 is cross-sectional view of the reaction tube constituting a tubular reactor to be used in the present invention; Fig.3a being a circular cross-sectional view; and Fig.3b being an annular concentric cross-sectional;

10       Fig.4 is a longitudinal cross-sectional view illustrating a basic structure of the tubular reactor having an annular concentric cross-section to be used in the present invention;

15       Fig.5 is a longitudinal cross-sectional view illustrating a basic structure of the tubular reactor consisting of coil-type reaction tubes to be used in the present invention; Fig.5a being a schematic longitudinal cross-sectional view illustrating a single tubular reactor; and Fig.5b being a schematic longitudinal cross-sectional view illustrating multiple tubular  
20       reactors;

25       Fig.6 is a longitudinal cross-sectional view illustrating a basic structure of the tubular reactor consisting of multiple reaction tubes to be used in the present invention; Fig.6a being a schematic longitudinal cross-sectional view of the tubular reactor with a pH-

controlling means that is provided separately therefrom;  
and Fig.6b being a schematic longitudinal cross-sectional view of the tubular reactor with a pH-controlling means that is combined therein;

5        Fig.7 is a longitudinal cross-sectional view illustrating a basic structure of the shell-tube heat exchanger-type tubular reactor consisting of multiple reaction tubes to be used in the present invention; Fig.7a being a schematic longitudinal cross-sectional  
10       view of the tubular reactor with a pH-controlling means that is provided separately therefrom; and Fig.7b being a schematic longitudinal cross-sectional view of the tubular reactor with a pH-controlling means that is combined therein; and

15       Fig.8 is an example of the microscopic photograph for a hydrous zirconia sol prepared according to the method of the present invention.

#### Detailed Description of the Invention

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The preferred embodiments of the present invention will be described in detail with reference to the annexed drawings.

25       Fig.1 shows a schematic drawing illustrating a tubular reactor consisting of one reaction tube in order

to represent the major functions of the reactor. The tubular reactor(1) represented as one of the basic construction has a double-pipe heat exchanger which consists of a reaction tube(2) and a space for the flow  
5 of a heating medium(7).

The heating medium(7) for heating the aqueous solution of a zirconium salt(3a) flowing in the reaction tube(2) may be any kinds of materials such as heating medium oil, liquid- or vapor-phase water or alcohol, and  
10 the like.

The effect of the present invention may be obtained, even though the heating medium flows in the reaction tube of the tubular reactor and the aqueous solution of the zirconium salt flows outside the reaction tube.  
15 However, it is more preferable that the aqueous solution of a zirconium salt(3a) flows in the reaction tube(2) and the heating medium flows outside the reaction tube(2) to uniformly maintain the flow of the reactants and the reaction conditions. The tubular reactor(1) may  
20 be installed in any direction for the aqueous solution(3a) of a zirconium salt to flow in a horizontal, vertical or diagonal direction.

Although the mechanism to prepare a hydrous zirconia sol(6) from the aqueous solution of a zirconium salt(3a)  
25 as a raw material of a hydrous zirconia has not been

well known, the generation of a hydrous zirconia sol is considered to be related with the hydrolysis of a zirconium salt and the precipitation of hydrous zirconia particles. As illustrated in the said formula of hydrolysis, the hydrolysis may also be considered to initiate at least partially in the course of provision of the said zirconium aqueous solution.

The temperature( $T$ ) of the aqueous solution of a zirconium salt(3a) in the reaction tube(2) at a certain distance( $z$ ) from the inlet of the reaction tube(2) in the tubular reactor(1) is changed as illustrated in Fig. 2. When the aqueous solution of a zirconium salt(3a) is continuously supplied to the inside of the reaction tube(2) through the inlet of the reaction tube( $z = z_i = 0$ ) at the inlet temperature( $T_i$ ) and heated to above the precipitation temperature( $T_p$ ) at a certain distance( $z = z_p$ ) by the heating medium(7), the zirconium salt in a supersaturated state begins to precipitate since the solubility of the zirconium salt becomes lowered with the increase of temperature. Here, " $z$ " is the distance from the inlet at the reaction tube, and the temperature  $T(z)$  at a distance  $z$  increases with  $z$  from the inlet temperature( $T_i$ ) at  $z_i = 0$ . The nuclei of the precipitate, in other words, the major component of the precipitated particles may be the zirconium salt itself or the



hydrous zirconia generated by the hydrolysis. When the reaction mixture is heated to above  $T_F$ , spherical particles(4) grow in size with the agglomeration of the nuclei particles or with the continuous precipitation of the nuclei on the surfaces of the growing particles(4).

Since the growth of the particles proceeds instantly in a complicated manner, changes in their composition or the rapid transformation within the reaction mixture(5) can hardly be understood in a physical or a chemical point of view.

When the solution (3a) as a starting material is heated to the outlet temperature( $T_o$ ) that is nearly equal to or less than the solution's boiling point as it flows toward the outlet( $z = z_o$ ) through the reaction tube(2), the generation and growth of the precipitated particles(4) are completed and discharged in the form of a suspension(3b) through the outlet of the reaction tube. The suspension(3b) of particles, in a state of sol, is mixed with a pH control agent(12) in a mixer(13) unless otherwise provided, and then is discharged as a reaction product(6) in a state of sol having an adequate pH range in about 5~12. The term "sol" herein means a suspension in which the precipitated particles(4) prepared thereby are dispersed in a solution without being subject to gelation due to particle agglomeration.

In order to prepare the spherical hydrous zirconia particles with an average diameter of nanometer-size and a small particle size distribution according to the present invention, it is preferable for the aqueous solution(3a) of a zirconium salt to flow in a laminar state, that is, a state without any noticeable turbulence within the reaction tube(2). Especially, it is important that the laminar flow having a velocity gradient(8) formed by the pressure difference between the inlet and the outlet of the reaction tube and by the shear stress due to a resistance of the inner wall of the reaction tube should be substantially maintained at least until the temperature reaches around the precipitation temperature( $T_p$ ) initiating the formation of nuclei of the precipitated particles(4).

The term "precipitation" herein means a phenomenon that the nuclei of zirconium salts or hydrous zirconia begin to form, even though they cannot be visually confirmed. The precipitation temperature( $T_p$ ) and the corresponding distance( $z_p$ ) for initiating precipitation cannot be precisely determined. They surely are, however, present between the inlet temperature( $T_i$ ) that the aqueous solution of a zirconium salt is supplied and the outlet temperature of the reaction product( $T_i < T_p < T_o$ ).

Since the aqueous solution of a zirconium salt may initiate a precipitation and gelation of particles followed by sedimentation even at around the room temperature, the preferable inlet temperature( $T_i$ ) of the aqueous solution of a zirconium salt is not more than 25°C.

It is necessary to set the outlet temperature( $T_o$ ) of the reaction product so as to fully generate and grow the precipitated particles in the suspension(3b). According to the present inventors' examination, it was confirmed that there was no problem in preparation of the precipitated hydrous zirconia particles, though the reaction mixture was heated to the boiling point( $T_b$ ) of the aqueous solution of a zirconium salt or the temperature range of about  $70^\circ\text{C} < T_o < T_b$ .

When the reaction mixture is heated to its boiling point( $T_b$ ), many bubbles are formed in the reaction mixture. However, when the precipitated particles are fully generated and grown in the reaction tube according to the present invention, there occurred no problem in the quality of the obtained hydrous zirconia sol in spite of a severe turbulences induced by the bubbles generated near the outlet of the reaction tube.

It is noted that  $T_b$  should be decided by considering the pressure in the reaction tube and the composition of

the reactant.  $T_b$  may be raised as the pressure in the reaction tube is increased. Among the solvents constituting the aqueous solution of a zirconium salt, most high molecular-weight alcohols may have a boiling point of not less than  $100^\circ\text{C}$ . In this case,  $T_o$  may be in the range of  $100^\circ\text{C} < T_o < T_b$ . It is, however, preferred to maintain  $T_o$  in the range of about  $70\sim 100^\circ\text{C}$ , because there is no problem in attaining the present invention even at  $T_o$  of not higher than about  $100^\circ\text{C}$ .

10        The materials of the reaction tube wherein the reaction mixture flows may be selected from metal materials such as carbon steel and stainless steel, inorganic materials such as graphite, low heat transfer materials such as quartz and glass(for example Pyrex).

15        It is also important to maintain as uniformly as possible the residence time of the reaction mixture in the reactor to prevent the increase of a size distribution and the deterioration of product quality that can be attributed to the distribution of the residence time. Accordingly, it is required that the reactor consisting of the reaction tube(s) should be also designed so that a partial stagnation or an excessive distribution of the residence time may not possibly occur throughout the flow of the reaction mixture.

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According to the present invention, the average flow velocity ( $u$ ) of the said aqueous solution of a zirconium salt is preferably regulated at an average residence time of the solution in the said reactor so as to be within about 1~60 seconds.

There is no limitation in a cross-sectional shape of the reaction tube in which the reaction mixture flows. However, the cross-sectional shape of the reaction tube is preferably circular (inner diameter:  $D$ , Fig.3a) or concentric annular (diameters of annular region:  $D_1$  and  $D_2$ , Fig.3b) to minimize the non-uniform flow, local stagnation, turbulence and to uniformly heat the reactant in the reaction tube(s).

Fig.4 illustrates a structure of the tubular reactor wherein a cross section of the reaction tube is concentric annular(Fig.3b). The aqueous solution of a zirconium salt (3a) in the reactor flows in the space of the annular region and the heating medium(7,7') flows in and out the concentric reaction tube at the same time unlike the reaction tube having a circular cross section as illustrated in Fig.1. Accordingly, the aqueous solution of zirconium salt(3a) can be more uniformly and effectively heated.

It is required that the cross-sectional area of the reaction tube should not be excessively large in order

to heat as uniformly as possible the reactant flowing in the reaction tube. When both the inner diameter of the reaction tube having a circular cross section and the equivalent diameter  $[(D_2^2 - D_1^2)^{1/2}]$  of the annular region of the concentric tubes are represented as 'D', the value of D is preferably about not more than 5 cm, more preferably, not more than about 3 cm. If the value of D is too low, it is difficult to control the flow of the reactant and to make the precipitated hydrous zirconia particles move freely entrained with the flow. Accordingly, the value of D is preferably at least about 0.01 cm.

The solvent used for the aqueous solution of a zirconium salt in the said reaction tube should satisfy the following formula when measured at 25°C to satisfy at the same time both the flow characteristic and the uniform heating of the reactant according to the present invention:

$$\rho \cdot u \cdot D / \mu \leq 2,000$$

wherein,  $\rho$  represents the density(g/cm<sup>3</sup>) of the solvent,  $\mu$  the viscosity(g/cm·sec) of the solvent,  $u$  the average flow velocity(cm/sec) of the solvent, and D the diameter or equivalent diameter of the cross section. Further, there is no problem even in a low value of not more than 1,000 in which the characteristic of the laminar flow

dominated by shear stress is remarkably appeared.

It is predicted, from the viewpoint of the fluid dynamics, that the small size distribution of colloidal particles can hardly be controlled when the velocity  
5 gradient(8) is formed along the radial direction of the reaction tube owing to a shear stress applied in a laminar flow unlike the conventional static reaction system. It thus has been anticipated that the size distribution of the precipitated particles(4) is  
10 necessarily large in accordance with the distribution of the residence time of the reactant due to the velocity gradient(8) in the reaction tube. On the contrary to this anticipation, it was surprisingly found that the particles of the hydrous zirconia sol(6) prepared  
15 continuously by using the tubular reactor according to the present invention has a small size distribution and the agglomeration of the particles obtained thereby is unnoticeable.

In the meanwhile, it is not necessary to maintain  
20 the value of  $p \cdot u \cdot D / \mu$  too low. When the average flow velocity( $u$ ) in a given tubular reactor is maintained very low, the heat duty to be supplied to the reactant is reduced. However, it is not necessary to reduce the value of  $u$  sacrificing the preparation rate, since the  
25 rate of heat transfer may be lowered in the reaction

tube leading thereby to more difficulty in heating of the reactant. Therefore, the operational conditions of the reactor according to the present invention are preferably decided by considering the quality of the prepared hydrous zirconia sol, heating of the reactant, preparation rate, and the like.

The concentration of the aqueous solution of a zirconium salt used in the present invention, that is, the concentration of zirconium oxychloride widely used as a precursor of zirconia is not more than about 0.5 mole/l, preferably not more than about 0.2 mole/l. When the concentration of the zirconium salt is more than 0.5 mole per liter, the heating of the precursor aqueous solution in the reaction tube results in a gelation of particles upon the formation of hydrous zirconia particles in a high concentration. Accordingly, the quality of the hydrous zirconia excessively deteriorates and the flow of the reactant becomes difficult, thereby the continuous operation being impossible.

The low concentration of the aqueous solution of a zirconium salt does not cause any problems in performing the present invention. However, when the concentration is too low, the preparation rate of the desired hydrous zirconia is excessively lowered. Accordingly, the concentration of aqueous solution of a zirconium salt is



preferably not less than about 0.001 mole/l.

In general, when the concentration of the aqueous solution of a zirconium salt is low, it is discovered that an average diameter of the prepared hydrous zirconia is reduced. However, this is not always the case. According to the present inventors' examination, the average diameter of the hydrous zirconia continuously prepared in the tubular reactor is smaller than that of the hydrous zirconia prepared by heating the aqueous solution of a zirconium salt in a static state, even though the concentrations are the same in both cases.

According to the present invention, since the average diameter, the size distribution and the particle's shape of the prepared hydrous zirconia are dependant on the concentration of aqueous solution of a zirconium salt, the composition of the solvent, the structure and the operational conditions of the reactor, the heating rate of the reactant, pH adjustment and the like, all the conditions relating to the precipitation are necessarily optimized.

As illustrated in the said hydrolysis formula, since the suspension(3b) in a state of sol primarily prepared in the tubular reactor according to the present invention contains many  $H^+$  and  $Cl^-$  ions and is a acidic

solution having very low pH, it is required to be deionized. Further, the state of dispersion of the colloidal particles is also dependent on pH value of the solution. Therefore, it is often necessary to control the pH value of the suspension(3b) so that the pH value of a hydrous zirconia sol(6) may be in a range of about 5~12 for the purpose of post-processing steps such as separation of byproducts(ions) out of the hydrous zirconia, and concentration and/or calcination and crystallization of hydrous zirconia; and of securing the quality of zirconia particles.

Various methods may be employed to control the pH value of the suspension(3b).

Firstly, it is possible to control the said pH value by continuously or intermittently adding an ammonia solution as a pH control agent to the suspension(3b) just before or after the suspension leaves the reaction tube(2). There may be used, as an ammonia aqueous solution, an ammonia( $\text{NH}_3$ ) dissolved in a distilled water, or an ammonia dissolved in a water-alcohol mixture used as a solvent for the aqueous solution of a zirconium salt.

Otherwise, the suspension(3b) leaving the reaction tube(2) may be mixed with a pH control agent(12) in a separate mixer(13), as illustrated in Fig.1. The

mixer(13) may be a stirred-type vessel equipped with an agitation means or a vessel without with an agitation means wherein a suspension(3b) and a pH control agent(12) are mixed with each other in a just flowing state. Alternatively, as illustrated in Fig.4, they may be mixed before or after the outlet of the reaction tube of the tubular reactor or in the outlet tube of the suspension(3b) without with an agitation means. In addition to this method, it is also possible to control the pH value of a hydrous zirconia sol by continuously or intermittently adding a pH control agent(12) to the reservoir storing the suspension(3b) leaving the tubular reactor. The ammonia concentration of an ammonia aqueous solution is not specifically limited, but about 0.01~10N of ammonia water is preferable.

Secondly, it is possible to control the said pH value of the suspension(3b) by contacting a gas containing an ammonia( $\text{NH}_3$ ) as a pH control agent with the suspension(3b). In this case, it is necessary to more sufficiently perform a gas-liquid contact between the suspension(3b) and the gaseous pH control agent(12). For the purpose of the contact, there may be employed various contact means as a gas-liquid mixer(13) as follows: (i) a scrubber contacting a gas with the reactant by spraying the reactant into numerous small

droplets, (ii) a distillation column, (iii) a means allowing to introduce an ammonia-containing gas to the bottom of the reservoir of the reaction output (suspension) by distributing the ammonia-containing gas in the form of small bubbles, and the like. There may be used as an ammonia-containing gas a pure ammonia gas or an ammonia gas mixed with an inert gas such as air, nitrogen, argon and helium, which does not react with both ammonia and the reaction output at the room temperature.

Thirdly, it is possible to control the said pH value of the suspension(3b) by preliminarily mixing the aqueous solution of a zirconium salt(3a) with ammonium ion-producible materials such as urea( $\text{CO}(\text{NH}_2)_2$ ), cerium diammonium nitrate ( $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ ) and yttrium nitrate ( $\text{Y}(\text{NO}_3)_3$ ), and then introducing the mixture to the reactor so as to automatically control the pH value of the aqueous solution in almost parallel with the precipitation in the reaction tube(2).

At least two methods among the said three methods are combined to control the pH value of a hydrous zirconia sol prepared according to the present invention.

As long as the reactor geometry and the operational conditions of the reactor are optimized in performing

the present invention, there are no problems in terms of the agglomeration or particle size distribution of the hydrous zirconia particles obtained thereby. However, when it is practically difficult to optimize lots of operational conditions for a given reactor, the problems of the agglomeration or particle size distribution of the hydrous zirconia particles can also be reduced by additionally applying a dispersion agent thereto.

The dispersion agents to be used for this purpose are OH group- or COOH group-containing aqueous organic compounds. Among these, the organic compounds having higher boiling point than that of a solvent are preferable. The dispersion agents having relatively high molecular weight may be selected from at least one of hydroxy-propyl methyl cellulose, hydroxy propyl cellulose, sodium oleate, potassium ethylxanthate, poly(acrylic acid), polyvinyl alcohol, and polyoxyethylene nonionic surfactant. The dispersion agents having relatively low molecular weight may be selected from at least one of diol alcohols such as ethylene glycol, propylene glycol and 2-methyl-1,3-propanediol or multi-valent alcohols such as glycerol; and carboxylic acids containing OH group such as tartar acid, citric acid, malic acid and lactic acid.

The amount of the dispersion agent to be used is

dependent on the concentration of the aqueous solution of a zirconium salt, the composition of the solvent, the kind of the dispersion agent selected and the like. But it may be used in a range of about 0.05g~20g on the basis of one liter of the aqueous solution of a zirconium salt.

The tubular reactor to be used for continuous preparation of a hydrous zirconia sol according to the present invention can have various types.

At first, the reactors may have a straight-type as illustrated in Figs.1 and 4 and may have a coil-type as illustrated in Fig.5. However, the vapor-phase heating medium(7a) may be preferably employed in the coil-typed reaction tube to obtain more uniform heating and higher heat transfer effect.

The cross sectional area or the value of  $D$  of a reaction tube(2) may be uniform along the flow length direction( $z$ ) of the reactant. However, the cross sectional area may be increased from the inlet toward the outlet along the length direction without causing any problems.

The reactor(1) may have one reaction tube(2) as illustrated in Figs.1 and 4, or may have more than one reaction tube(2) as illustrated in Figs.5b, 6 and 7. For example, it is estimated that the productivity of a

hydrous zirconia sol in the tubular reactor(1) having two reaction tubes(2)(Fig.5b) will be approximately doubled than the productivity in the tubular reactor(1) having one reaction tube(2)(Fig.5a). However, it is  
5 required that the flowing state or the flow rate of the reactants should not be differentiated in each of the multiple reaction tubes.

Alternatively, Figs.6a and 6b represent the schematic longitudinal cross-sectional views of the  
10 tubular reactors(1) with multiple straight-type reaction tubes(2). In these reactors, the aqueous solution of zirconium salt(3a) is divided and supplied to the reaction tubes(2), heated by the heating medium(7) flowing outside the reaction tube(2) to produce the  
15 suspension(3b), and then optionally mixed with a pH control agent(12) in the mixer(13) to obtain a hydrous zirconia sol(6) having adequate pH.

If necessary, the said mixer(13) may be separately installed or combined to the tubular reactor(1)  
20 regardless of the number of reaction tube(2), as illustrated in Figs. 6a and 6b.

As illustrated in Figs.7a and 7b, conventional shell-and-tube type heat exchangers, which have widely  
25 been used in various chemical plants, can be utilized

for the tubular reactors(1) of Figs.6a and 6b.

The heating medium(7) may be devised to flow in a single path in the shell side as illustrated in Fig. 7a in order to use such a shell-and-tube type heat exchanger in the present invention. Alternatively, as  
5 illustrated in Fig.7b, the shell side may be partitioned into several sections by installing multiple partition plates or baffles(11) so that various kinds of or various temperatures of heating mediums(7', 7'') could be  
10 utilized through multiple inlets(7'a, 7''a) and outlets(7'b, 7''b).. This allows the aqueous solution of a zirconium salt (3a) in the reaction tube(2) to pass through multiple heating zones, whereby the heating condition along the flow distance(z) can be more finely  
15 controlled. Although not illustrated in the figures, such system can yield the same effects in preparing hydrous zirconia sol(6) as when connecting in series multiple numbers of tubular reactors that are heated respectively at different conditions.

20 In the meanwhile, as illustrated in Fig. 7b, a separate zone for protecting the temperature of the aqueous solution of a zirconium salt (3a) against the heating medium may be provided in the inlet shell of the reaction tubes(2) by additionally installing a partition  
25 plate(11') in the shell of the reactor. Allowing heat



not to be transferred from the high-temperature heating medium(7) toward the tube plate(9a) at the feed inlet side supporting multiple reaction tubes(2), the temperature protection zone prevents the aqueous solution of a zirconium salt (3a) supplied into the reactor(1) from being heated by the tube-supporting plates(9a) and precipitated before being introduced into the reaction tubes(2). Heating of the tube plate(9a) of the feed inlet side can be prohibited by allowing a cooling medium(10) having a lower temperature than the precipitation temperature ( $T_p$ ) to pass through the temperature protection zone.

Although all examples not being illustrated herewith, various types of heat exchangers equipped with multiple heating tubes can be employed for practical application of the present invention.

As stated in the above, the shapes of the hydrous zirconia particles constituting a hydrous zirconia sol continuously prepared according to the present invention are mostly spherical. The shapes can be confirmed by a high magnification scanning electron microscope(SEM) as illustrated in Fig.8. The term "spherical" in this specification means a circle or an oval having a major-minor axial ratio of the cross section of the particles in a range of about 1.0~1.5.

Further, the said hydrous zirconia particles exhibit very little agglomeration among them. According to the generally used image analysis method, the average diameter( $d_p$ ) of the hydrous zirconia particles is in the  
5 range of about 1~1,000 nm and the size distribution of the hydrous zirconia particles is as low as more than 90% of the particles have diameters in the range of  $0.5d_p \sim 2d_p$ .

Otherwise, most of these hydrous zirconia particles  
10 are amorphous. Departed from the present invention, these amorphous particles can be transformed to crystalline particles by subjecting them to the calcination at high temperatures, even though various the crystalline structures are possible depending on the  
15 calcination temperature.

The hydrous zirconia sol prepared is subjected to the post processing steps before it is used for the desired purpose. In general, the hydrous zirconia sol is subjected to washing and concentration steps through the  
20 separation method such as ultra filtration. In this washing process, the impurities contained in the hydrous zirconia sol can be removed by using water. This process may be performed before or after concentrating the sol.

The purified and concentrated hydrous zirconia sol  
25 can be used for various materials such as (i) electronic

materials or coating materials in the form of stabilized sol itself, (ii) functional ceramics or electronic materials in the form of monodispersed, nanometer-sized powder subjected to drying and/or calcination, (iii) 5 materials for catalysts or batteries/cells subjected to surface-modification by coating, (iv) functional ceramics or structural ceramics in the form of composite materials combined with other components, and the like.

Now, the preferred embodiments of the present 10 invention will be described in detail by the following Examples without limiting the scope of the invention in any way.

(Example 1)

15 0.2 mole of zirconium oxychloride and 1g of hydroxypropyl methyl cellulose are dissolved in one liter of the solvent mixture of 2-propyl alcohol and water (a molar ratio of 0.94) to prepare the aqueous solution of a zirconium salt. As illustrated in Fig. 5b, two coil- 20 typed reaction tubes having inner diameter of 9.5 mm and length of 5 m each and consisting of Pyrex glass are installed in a stainless steel vessel to form a condenser-typed tubular reactor. The aqueous solution of a zirconium salt is supplied to the said reaction tubes 25 at the temperature of about 10 °C at a flowing rate of

430 cc/min. A vapor-phase heating medium consisting of the heated water and ethanol (a molar rate of 1:1) is supplied to the inside of the said reactor (the outside of the reaction tube) at the temperature of 98 °C, and then condensed therein. As a result, the temperature at the outlet of the reaction tube may be 74 °C. The pH value of the suspension discharged from the outlet of two reaction tubes is controlled to be 9.1 by adding 0.8N-ammonia water in a mixer to continuously prepare a hydrous zirconia sol.

The hydrous zirconia particles are filtered off the obtained hydrous zirconia sol through a 20 nanometer-sized filter and then repeatedly washed with distilled water until ions of  $\text{Cl}^-$  are not detected. The hydrous zirconia particles are dried at the temperature of 85°C for 24 hours to observe the properties of the particles with SEM. The resultant hydrous zirconia particles are mostly spherical and do not exhibit agglomeration among them. It is confirmed that there are prepared the hydrous zirconia having size distribution as low as the diameter( $d$ ) of the particles is in the range of 116.2 nm  $\leq d \leq 262.7$  nm, the average diameter( $d_p$ ) is 193.5 nm, and the standard deviation is 32.4 nm.

The said hydrous zirconia particles are shown to be amorphous according to X-ray diffraction (XRD) analysis.

But, they are crystallized in the course of calcination at the temperature of not less than 400°C, although their crystalline structure is different depending on the temperature.

5        Zirconia particles are obtained after removing bounded water from the hydrous zirconia by the said calcinations process. In this calcination, the average diameter is 196.1 nm, but the size and the shape have been little changed and the agglomeration of the  
10       particles has not been newly found.

(Example 2)

0.04 mole of zirconium oxychloride and 0.6g of hydroxy-propyl cellulose are dissolved in one liter of  
15       the solvent mixture of 1-propyl alcohol and water (a molar ratio of 1.7) to prepare the aqueous solution of a zirconium salt. As illustrated in Fig. 7a, 37 stainless steel reaction tubes having inner diameter of 3.37 mm and length of 500 mm form a shell-tube heat exchanger  
20       type tubular reactor. The aqueous solution of a zirconium salt is supplied to the said reaction tubes at the temperature of about 8 °C at a total flowing rate of 1,150 cc/min. A vapor-phase heating medium obtained by  
25       said reactor (the outside of the reaction tube) at the

temperature of 84 °C, and then condensed therein. As a result, the temperature at the outlet of the reaction tube may be 78 °C.

5 The pH value is controlled to 5.6 by adding and mixing 2.0 N-ammonia water in a discharging tube of the suspension mixer to continuously prepare a hydrous zirconia sol.

10 Five (5) drops of the obtained hydrous zirconia sol are diluted with 10 cc of the distilled water to give a solution. One (1) drop of the solution is added to the carbon mount. The hydrous zirconia particles are dried at the temperature of 85°C for 10 hours to observe the properties of the particles with SEM. The resultant hydrous zirconia particles are mostly spherical and do  
15 not exhibit agglomeration among them. It is confirmed that there are prepared the hydrous zirconia having size distribution as low as the diameter(d) of the particles is in the range of  $36.4 \text{ nm} \leq d \leq 131.1 \text{ nm}$ , the average diameter( $d_p$ ) is 67.5 nm, and the standard deviation is  
20 16.1 nm.

(Example 3)

0.2 mole of zirconium oxychloride and 7g of polyvinyl alcohol are dissolved in one liter of the  
25 solvent mixture of 2-propyl alcohol and water (a molar

ratio of 0.94) to prepare the aqueous solution of a zirconium salt. As illustrated in Fig. 4, there is used a tubular reactor having an annular concentric cross-section, 300 mm of length and three(3) straight-type stainless steel tubes in scales of 1/4 inch, 3/8 inch and 3/4 inch, respectively. The said aqueous solution of a zirconium salt is supplied to an annular concentric zones of 1/4 inch and 3/8 inch reaction tubes at the temperature of about 10 °C at a flowing rate of 30 cc/min. The hydrocarbon-based heating medium oil heated to 95 °C is simultaneously supplied both inside the 1/4 inch-tube and between the 3/8 inch and 3/4 inch tubes against the flowing direction of the said aqueous solution of a zirconium salt so that the temperature of the suspension at the outlet of the reaction tube having annual concentric cross sections may be 82 °C. The said suspension is contacted with ammonia gas in a mixer to have 5.2 of pH, and thus a hydrous zirconia sol is continuously prepared.

Two (2) drops of the obtained hydrous zirconia sol are diluted with 10 cc of the distilled water to give a solution. One (1) drop of the solution is added to the carbon mount. The hydrous zirconia particles are dried at the temperature of 85°C for 10 hours to observe the properties of the particles with SEM. The resultant

hydrous zirconia particles are mostly spherical and do not exhibit agglomeration among them. It is confirmed that there are prepared the hydrous zirconia having size distribution as low as the diameter( $d$ ) of the particles is in the range of  $121.6 \text{ nm} \leq d \leq 287.2 \text{ nm}$ , the average diameter( $d_p$ ) is 213.5 nm, and the standard deviation is 30.8 nm.

The said hydrous zirconia particles are shown to be amorphous according to X-ray diffraction (XRD) analysis. But, they are crystallized in the course of calcination at the temperature of not less than  $400^\circ\text{C}$ , although their crystalline structure is different depending on the temperature.

Zirconia particles are obtained after removing bounded water from the hydrous zirconia by the said calcinations process. In this calcination, the average diameter is 211.1 nm, but the size and the shape have been little changed and the agglomeration of the particles has not been newly found.

20

### Industrial Applicability

The hydrous zirconia particles prepared according to the present invention are unexpectedly excellent in quality. The hydrous zirconia particles constituting a

25



hydrous zirconia sol are mostly spherical, have a small particle size distribution, that is, uniform diameter, and do not exhibit agglomeration among them. Particularly, these particles have an advantage that  
5 they do not exhibit agglomeration not only in a state of sol but also in the course of concentration and calcination.

The present invention provides a method for continuous preparation of a hydrous zirconia sol, which  
10 is feasible to be followed by separation and purification operations such as ultra filtration. Accordingly, the processes from the preparation of the hydrous zirconia sol to the separation and purification can also be continuously performed.

15 The tubular reactor to be used for continuous preparation of the hydrous zirconia sol according to the present invention has a conventional heat exchanger type, which is ordinarily used in normal chemical plants. Therefore, since the tubular reactor to be used  
20 in the present invention can be easily fabricated and can be assembled in various ways, there is no limit in applying the present invention to a commercial-scale bulk preparation.

Contrary to the method employing a conventional  
25 batch-type reactor or semi-continuous stirred-type

reactor, the method for continuous preparation of a hydrous zirconia sol according to the present invention can allow various operational parameters to be controlled in a certain range and thus contributes to remarkably improve the quality of a hydrous zirconia sol. 5 to be prepared or of the zirconia powder obtainable as a final product.

What is claimed is:

1. A method for continuous preparation of a well dispersed spherical hydrous zirconia particles with an average diameter( $d_p$ ) of 1~1,000 nm in the form of sol,  
5 which method comprises continuously supplying the aqueous solution of a zirconium salt at a concentration of 0.001~0.5 mole/l to a reactor consisting of one or more than two reaction tubes at a temperature less than  
10 about 25 °C, heating the said aqueous solution in the reactor(s) in a continuous flow state up to the boiling point or less, and then discharging the said solution through the outlet of the said reactor(s).

15 2. A method for continuous preparation of a hydrous zirconia sol according to Claim 1 wherein the said aqueous solution of a zirconium salt is heated to 70~100 °C in the reaction tube.

20 3. A method for continuous preparation of a hydrous zirconia sol according to Claim 1 wherein the said aqueous solution of a zirconium salt flows in the reaction tube having circular or annular concentric cross section.

25 4. A method for continuous preparation of a

hydrous zirconia sol according to Claim 1 wherein a solvent constituting the said aqueous solution of a zirconium salt is a mixture of water and at least one alcohol selected from a group consisting of ethyl  
5 alcohol, 1-propyl alcohol, 2-propyl alcohol and butyl alcohol; a mole ratio of the said alcohol/water mixture is 0.5~2.0; and a zirconium salt is selected from zirconium oxychloride, zirconium tetrachloride, zirconyl nitrate or zirconium sulfate.

10

5. A method for continuous preparation of a hydrous zirconia sol according to Claim 1 wherein the pH value of a hydrous zirconia sol is 5~12.

15

6. A method for continuous preparation of a hydrous zirconia sol according to Claim 1 wherein the average diameter( $d_p$ ) of the hydrous zirconia particles is about 10~250 nm.

20

7. A method for continuous preparation of a hydrous zirconia sol according to Claim 1 wherein the cross sectional shape of the reaction tube is circular or concentric annular form, and the value of D is 0.01~3 cm when a diameter of the said circle or an equivalent  
25 diameter corresponding to a concentric annular region is

"D."

8. A method for continuous preparation of a hydrous zirconia sol according to Claim 1 wherein a dispersant is added to the said aqueous solution of a zirconium salt at the concentration of 0.05~20 g/l.

9. A method for continuous preparation of a hydrous zirconia sol according to Claim 1 wherein at least one compound as stabilizer selected from a group consisting of halide (chloride and bromide), carbonate and nitrate of Y, Ca, Ce or Mg is further added to the aqueous solution of a zirconium salt so that the amount of the finally prepared oxides ( $Y_2O_3$ ,  $CeO_2$ , CaO or MgO) may be up to 30 mole % on the basis of  $ZrO_2$ .

10. A method for continuous preparation of a hydrous zirconia sol according to Claim 5 wherein at least one compound selected from a group consisting of urea ( $CO(NH_2)_2$ ), cerium diammonium nitrate ( $(NH_4)_2Ce(NO_3)_6$ ) and yttrium nitrate ( $Y(NO_3)_3$ ) is added to the aqueous solution of a zirconium salt to control the pH value of the solution.

11. A method for continuous preparation of a hydrous

zirconia sol according to Claim 5 wherein an ammonia aqueous solution is added to the reaction output discharging from the reaction tube to control the pH value of the output.

5

12. A method for continuous preparation of a hydrous zirconia sol according to Claim 5 wherein a gas containing ammonia ( $\text{NH}_3$ ) is contacted with the reaction output discharging from the reaction tube to control the pH value of the output.

10

13. A method for continuous preparation of a hydrous zirconia sol according to Claim 7 wherein the said dispersant is at least one selected from a group consisting of hydroxy-propyl methyl cellulose, hydroxy propyl cellulose, sodium oleate, potassium ethylxanthate, poly(acrylic acid), polyvinyl alcohol, polyoxyethylene nonionic surfactant, ethylene glycol, propylene glycol, 2-methyl-1,3-propanediol, glycerol, tartar acid, citric acid, malic acid and lactic acid.

15  
20

14. A method for continuous preparation of a hydrous zirconia sol according to claim 7 wherein the solvent of the aqueous solution of a zirconium salt in the said reaction tube satisfies the following formula when

25

measuring at the temperature of 25°C:

$$\rho \cdot u \cdot D / \mu \leq 2,000$$

wherein,  $\rho$  represents the density(g/cm<sup>3</sup>) of the solvent,  
 $\mu$  the viscosity(g/cm·sec) of the solvent,  $u$  the average  
5 flow velocity(cm/sec) of the solvent, and  $D$  the diameter  
or the equivalent diameter of the cross section.

15. A method for continuous preparation of a  
hydrous zirconia sol according to Claim 3 wherein the  
10 reaction tube is a coil type.

16. A method for continuous preparation of a  
hydrous zirconia sol according to Claim 3 wherein the  
said reactor is partitioned into multiple heating zones.

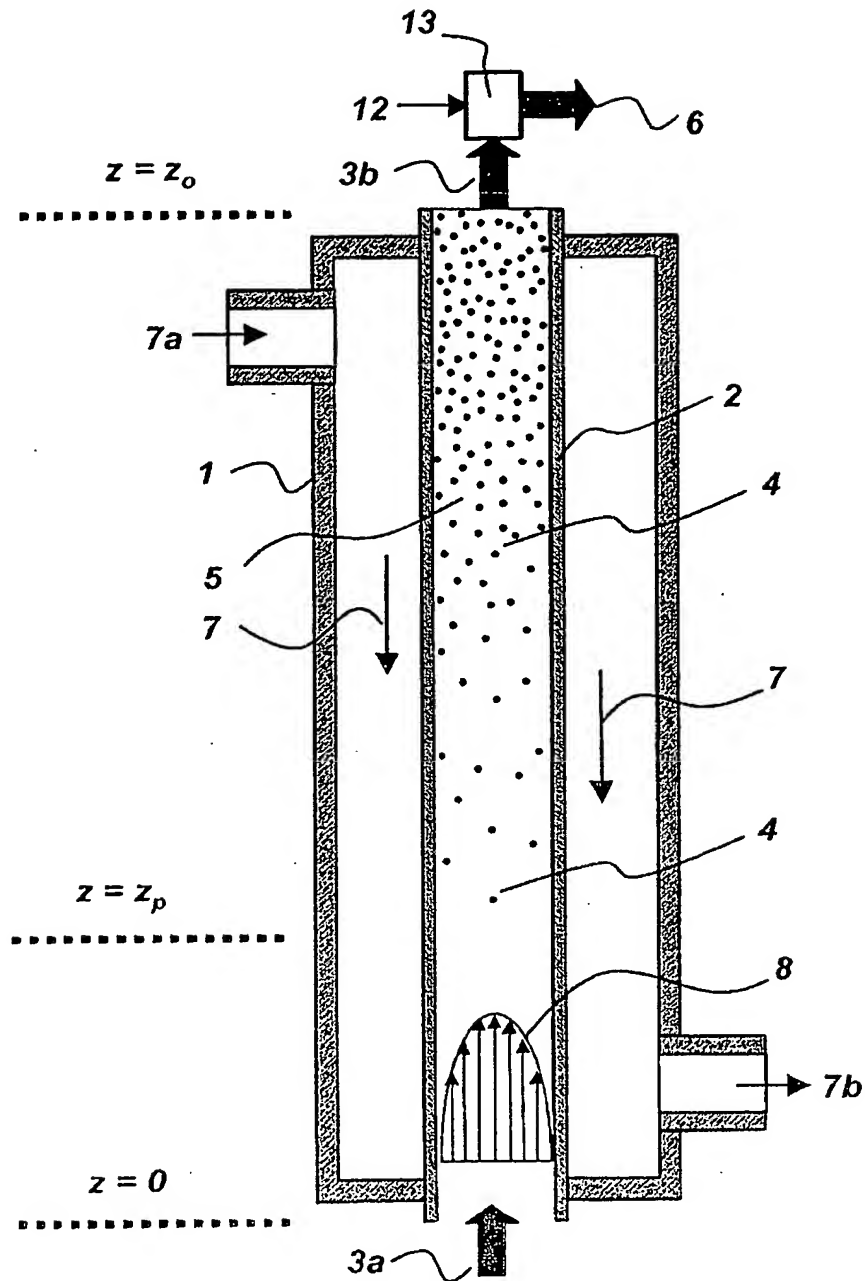
## Abstract

The present invention relates to a method a method for continuous preparation of a well dispersed spherical hydrous zirconia particles with an average diameter( $d_p$ ) of 1~1,000 nm in the form of sol solution, which method comprises continuously supplying the aqueous solution of a zirconium salt at a concentration of 0.001~0.5 mole/l to a reactor consisting of one or more than two reaction tubes at a temperature of less than 25 °C, heating the said aqueous solution in the reactor(s) in a continuous flow state up to the boiling point, and then discharging the said solution through the outlet of the said reactor(s).

Contrary to the method employing a conventional batch-type reactor or semi-continuous stirred-type reactor, the method for continuous preparation of a hydrous zirconia sol according to the present invention can allow various operational parameters to be controlled in a certain range and thus contributes to remarkably improve the quality of a hydrous zirconia sol to be prepared or of the zirconia powder obtainable as a final product.



Fig. 1



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Fig. 2

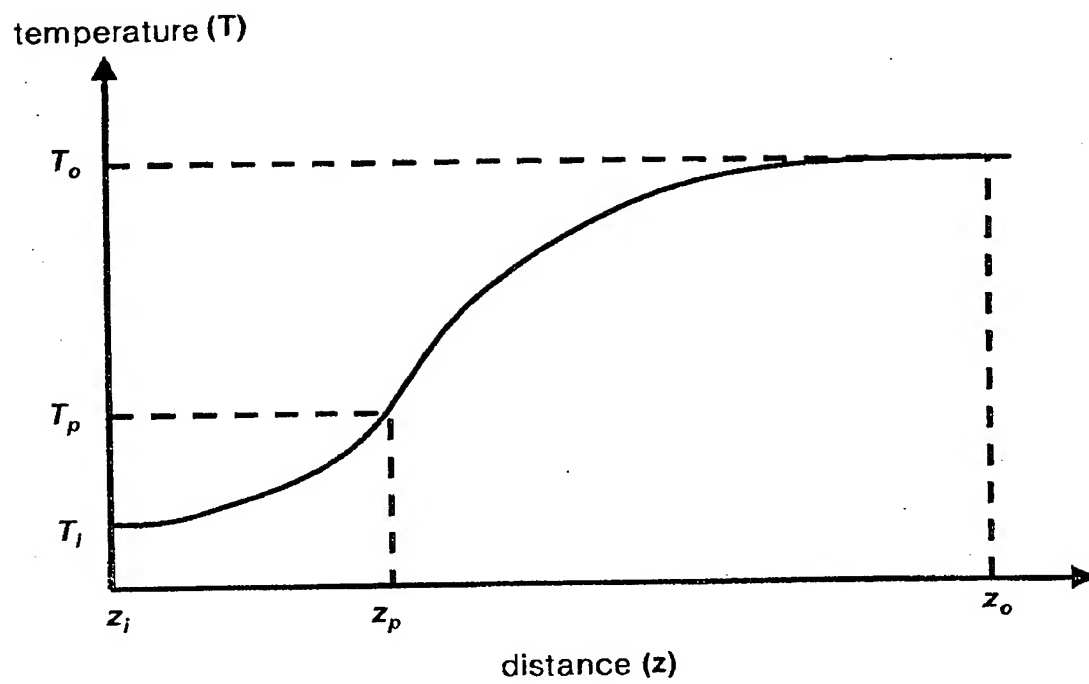


Fig. 3a

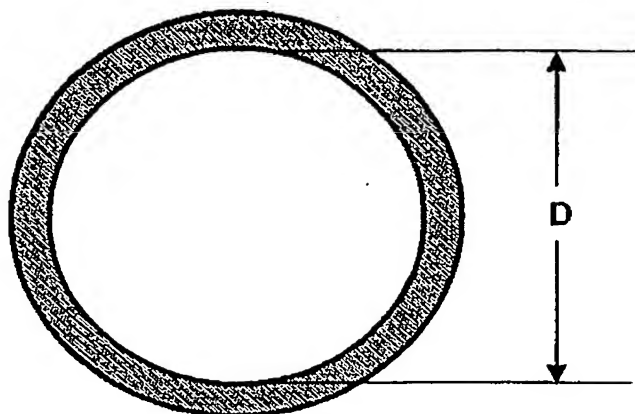


Fig. 3b

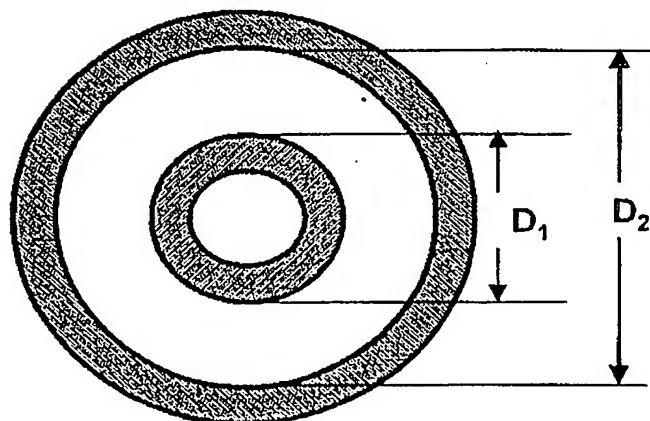


Fig. 4

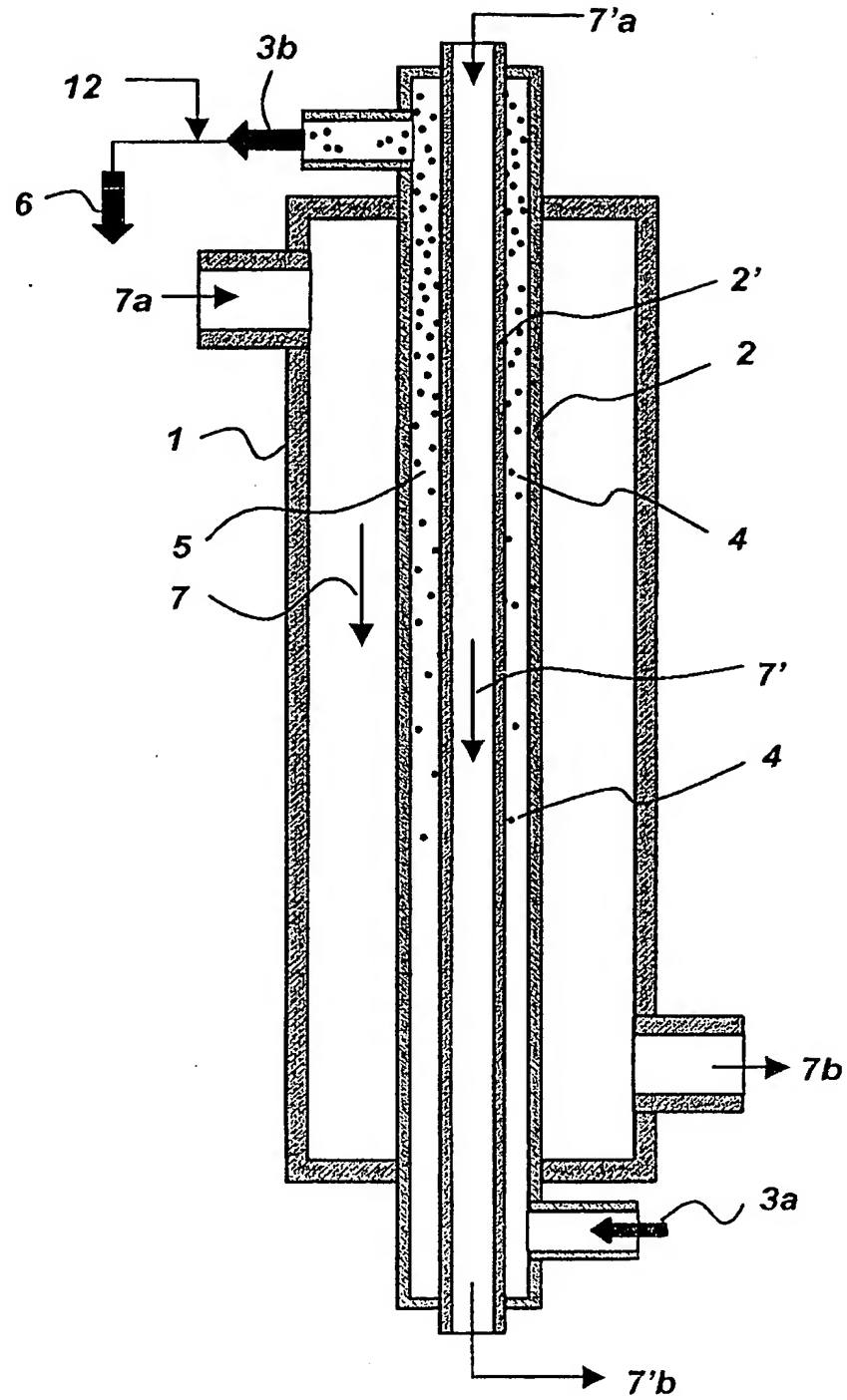


Fig. 5a

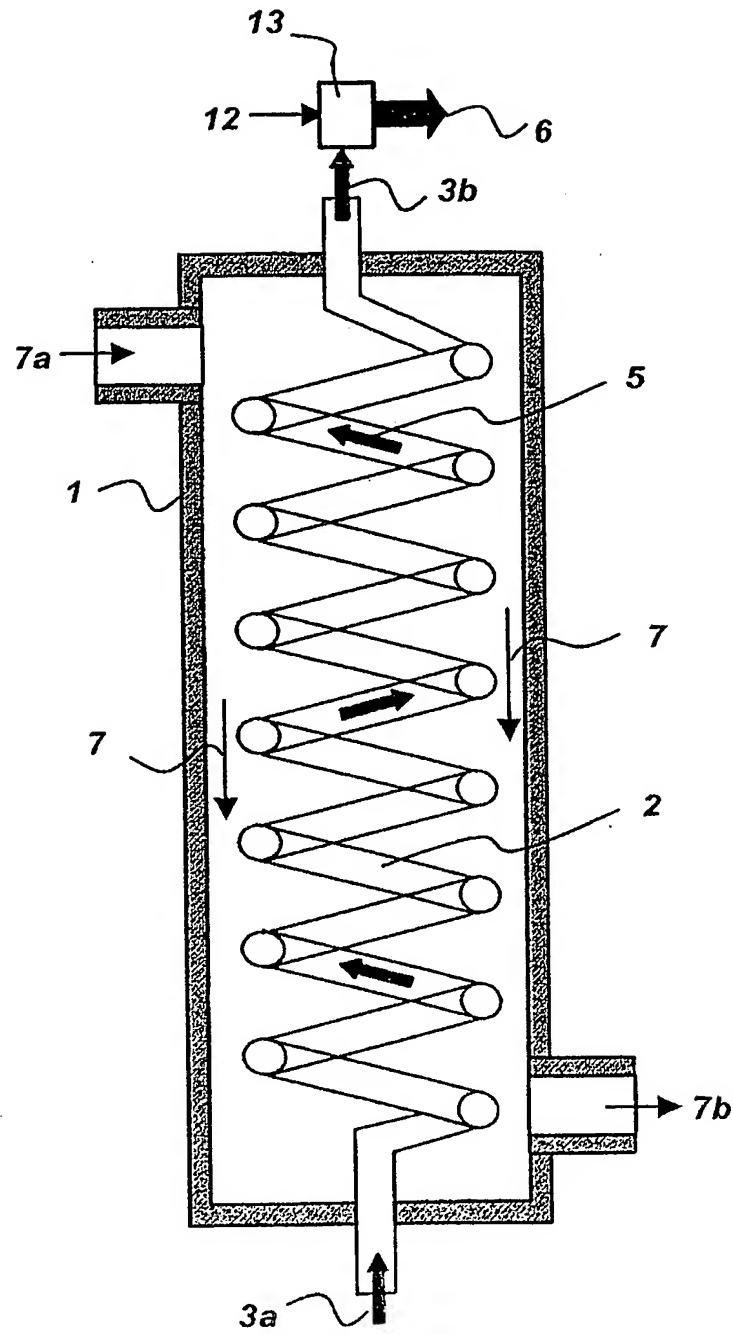


Fig. 5b

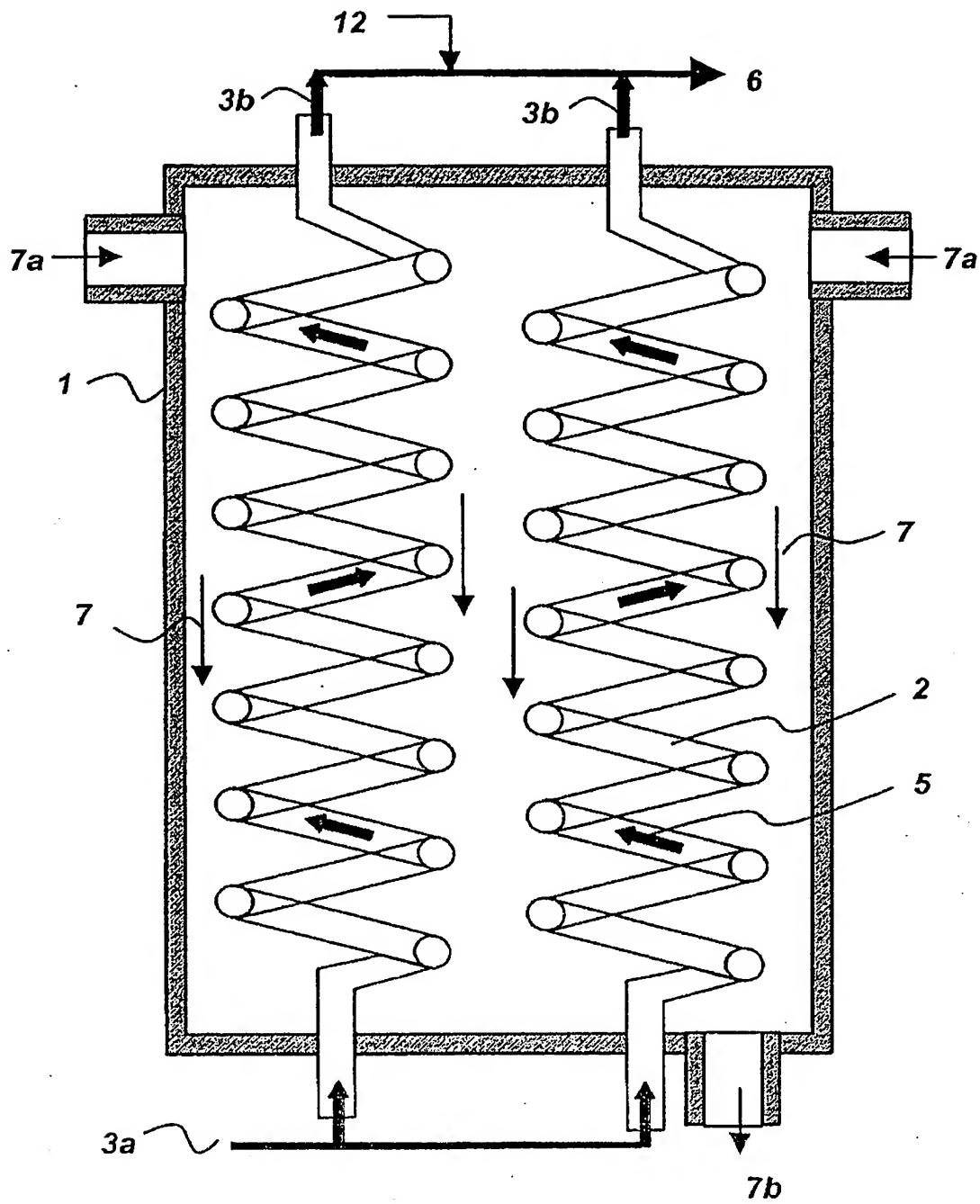


Fig. 6a

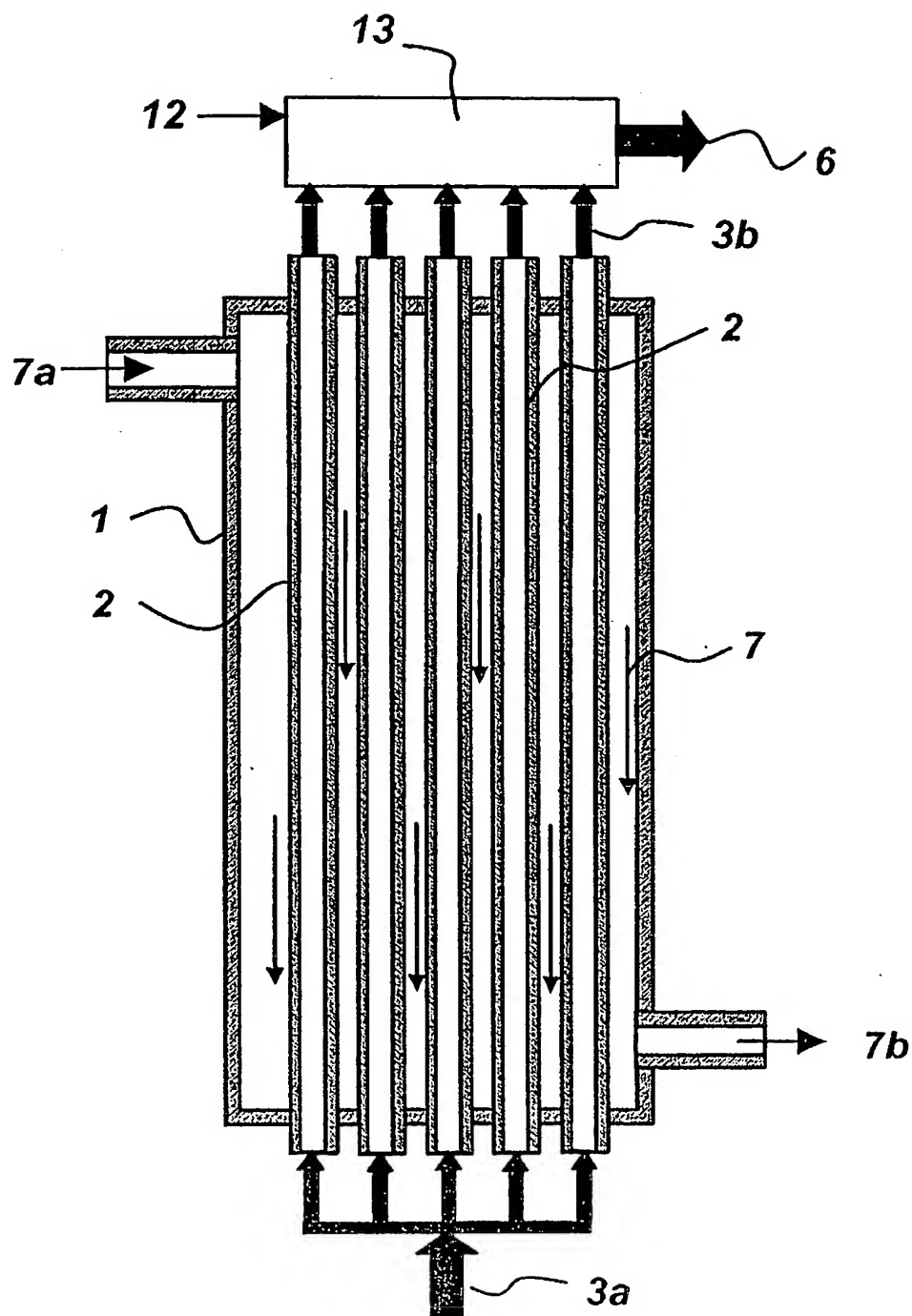


Fig. 6b

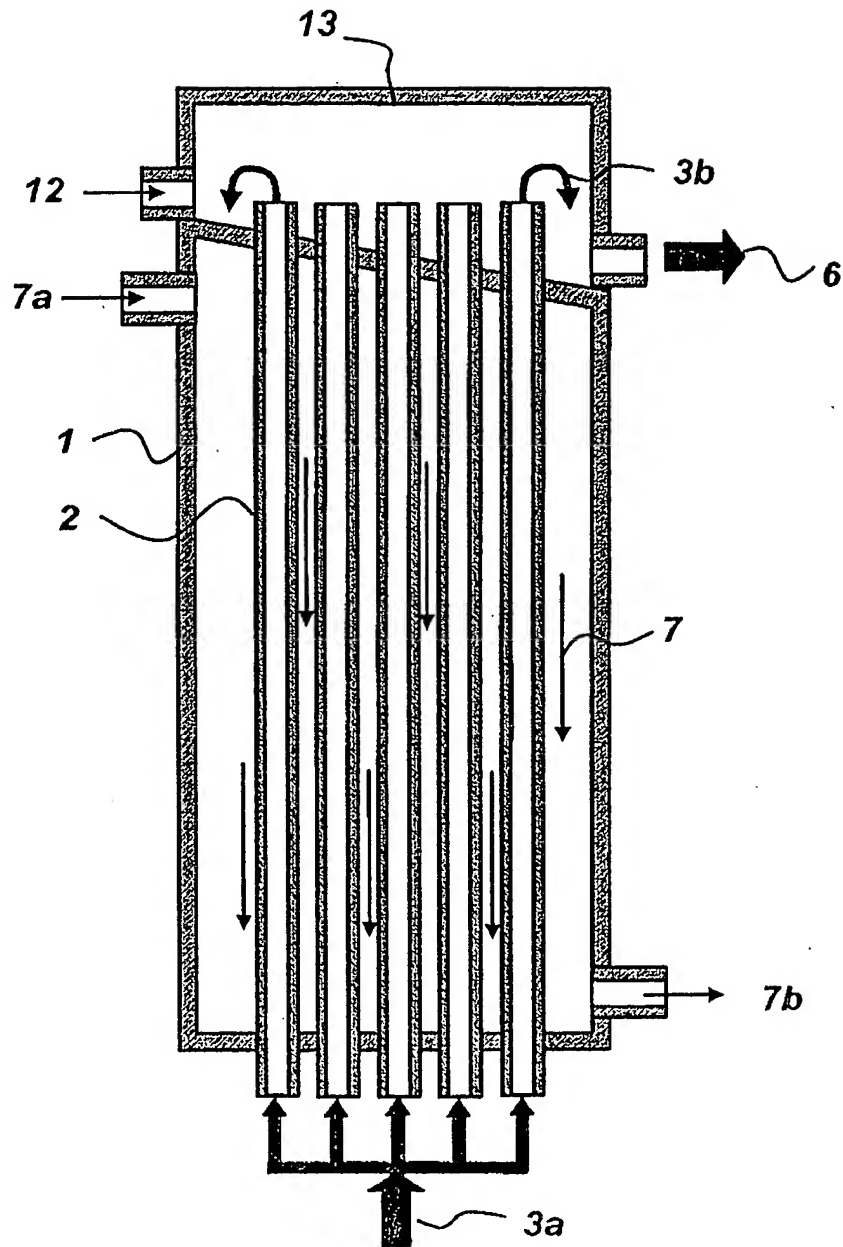




Fig. 7a

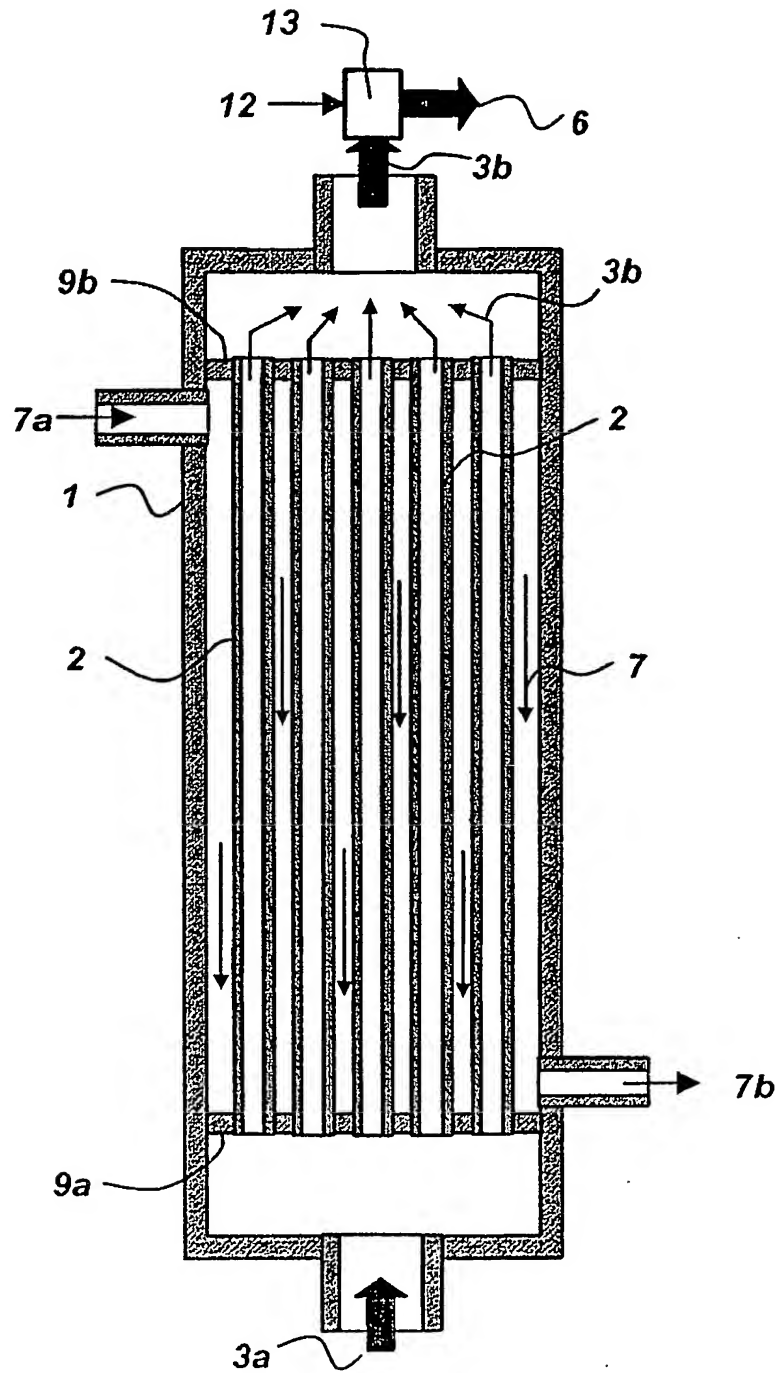


Fig. 7b

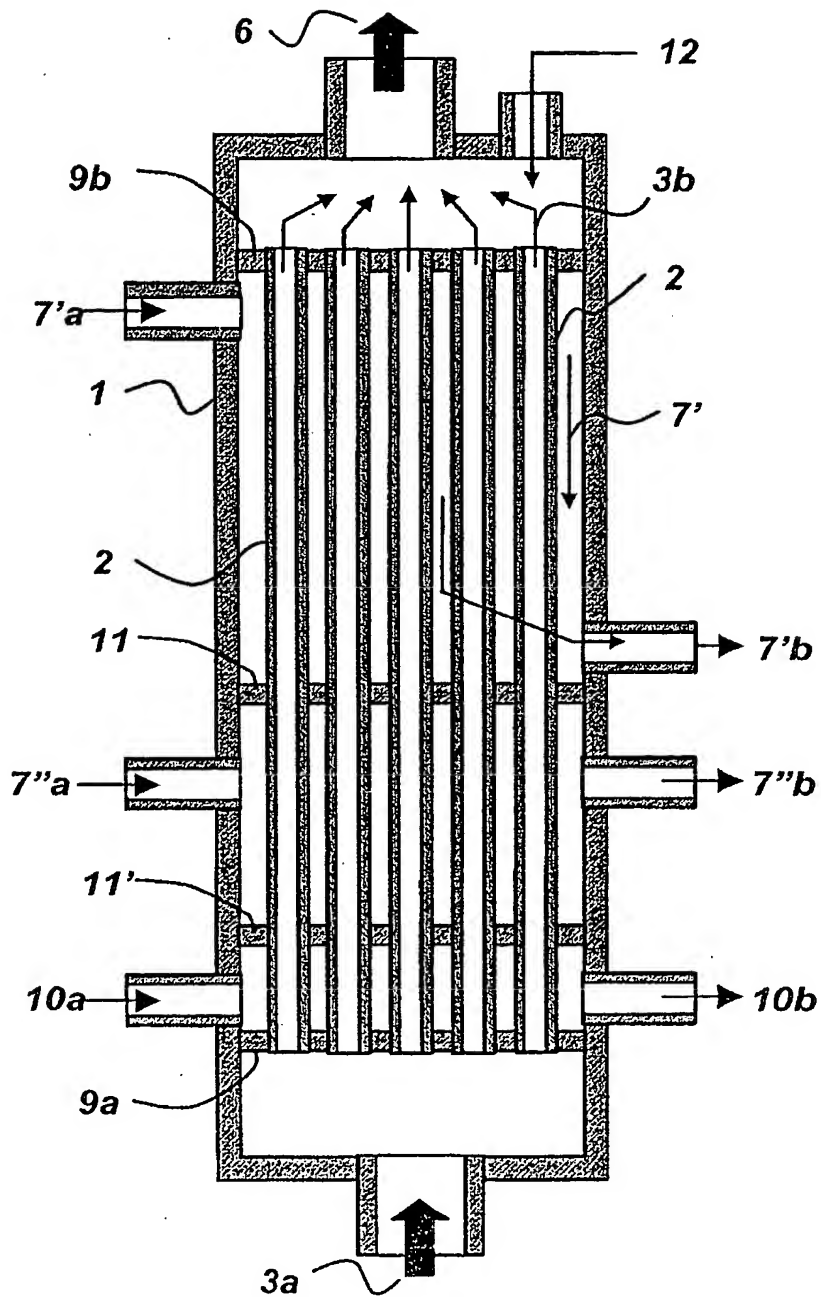
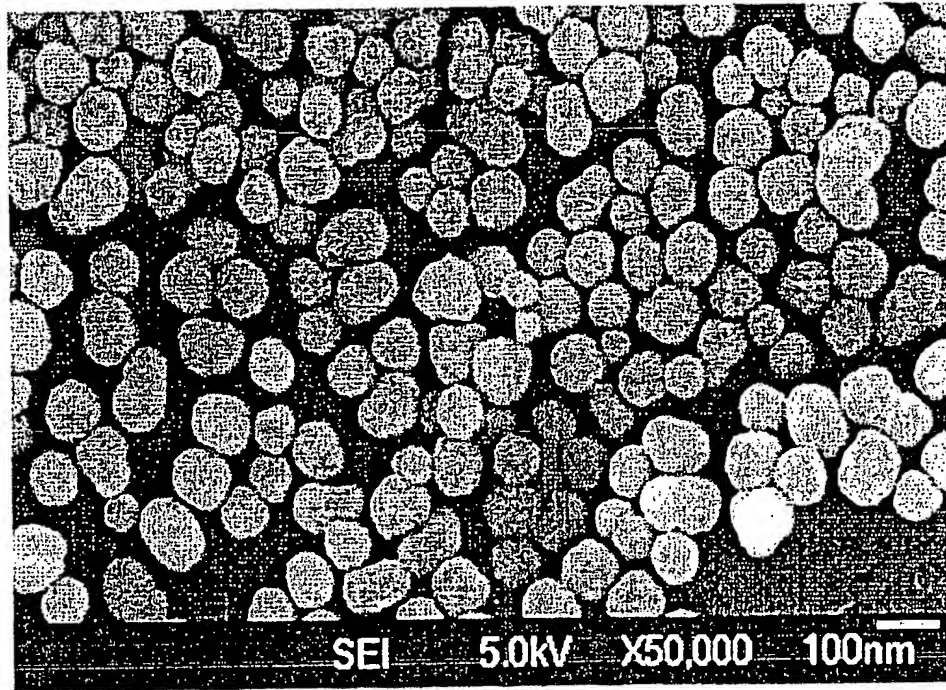


Fig. 8



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